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(54) Title of Invention: Sintered Ceramic Body and the Method of Manufacture Thereof

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Details of the Invention

1. TITLE OF THE INVENTION

Sintered Ceramic Body and the Method of Manufacture Thereof

2. RANGE OF CLAIMS

(1) Sintered ceramic body containing SiO_2 , CaO , P_2O_5 , Na_2O and MgO , where SiO_2 content is 20~70 wt%, the atomic ratio Ca/P is 1.0~5.7, the total content of SiO_2 , P_2O_5 and CaO is greater than 70 wt%, and the Na_2O and MgO contents are less than 2 wt% and less than 0.9 wt%, respectively.

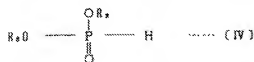
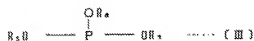
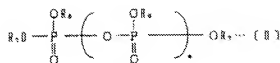
(2) Sintered ceramic body described in Claim 1 containing apatite crystals.

(3) Method of manufacture of sintered ceramic body containing SiO_2 , CaO , P_2O_5 , Na_2O and MgO , where SiO_2 content is 20~70 wt%, the atomic ratio Ca/P is 1.0~5.7, the total content of SiO_2 , P_2O_5 and CaO is greater than 70 wt%, and the Na_2O and MgO contents are less than 2 wt% and less than 0.9 wt%, respectively, in which at least one type of silicate esters shown by the general formula [I] is gelled in the presence of phosphate compounds and calcium compounds, and the resultant gel is dried, molded and then sintered.



($\text{R}_1 \sim \text{R}_4$ are hydrogen or radicals by the formula $\text{C}_x\text{H}_{2x+1}$ (OC_2H_4) $_y$ - < where $x = 1 \sim 5$, $y = 0 \sim 10$ >. All of $\text{R}_1 \sim \text{R}_x$ need not be hydrogen. n is $0 \sim 20$.)

(4) Method of manufacture described in Claim (3) where the phosphate compounds are at least one of the compounds shown by the general formulas [II], [III] or [IV].



(R5 ~ R9 are hydrogen, alkyl groups with 1 ~ 5 carbons, phenyl groups or aralkyl groups with 7 ~ 10 carbons, and m = 0 ~ 10).

- (5) Method of manufacture described in Claim (3) where the calcium compounds are calcium salts or at least one of the compounds shown by the general formula (V).



(R10 is an alkyl group with 1 ~ 5 carbons).

3. DETAILED DESCRIPTION OF THE INVENTION

[Industrial Field of Application]

This invention concerns the sintered ceramic body with biocompatibility which offers a variety of applications such as for synthetic tooth root and synthetic bone.

[Industrial Field of Application]

As synthetic tooth root and synthetic bone graft materials, various glass ceramics having SiO_2 , P_2O_5 and CaO as basic components are known. For example, reported in TOKKAI SHO57-191252 are crystal glasses for synthetic bone use structured with many apatite and wollastonite micro crystals scattered in the glass, at least 90% of which is composed of a mixture of MgO (1 ~ 7%), CaO (42 ~ 53%), SiO_2 (22 ~ 41%) and P_2O_5 (10 ~ 27%) with less than 10% of impurities. Also presented in TOKKAI SHO51-8970 are ceramics having SiO_2 , P_2O_5 , Na_2O , K_2O and MgO as the base components with occasional addition of fluorine. These compositions contain apatite crystals that contribute to biocompatibility. As the Ca/P atomic ratio of apatite crystal is approximately 1.67, it is desirable to approximate the composition to this ratio to increase the apatite crystal content. Conventional glasses with SiO_2 , P_2O_5 and CaO as base components did not fully vitrify at a Ca/P ratio below 5.7 and therefore products having even compositions could not be produced. In order to produce a glass ceramic having a Ca/P ratio close to that of apatite crystal composition, MgO was added at 1 ~ 7% (TOKKAI SHO57-191252), or MgO 2.9 ~ 30 wt% and Na_2O 2.7 ~ 20 wt% were added (TOKKO SHO51-8970). In these cases, MgO or Na_2O replaced CaO to lower the apatite crystal content and reduce the calcium silicate crystal content which normally contributes to improved strength. Further, the addition of Na_2O reduces the chemical stability of the sintered body.

[Problems This Invention Intends to Solve]

The purpose of this invention is to offer sintered ceramic body having an excellent strength and biocompatibility and the method manufacture of said sintered body.

[Means of Solving the Problem]

This invention is based on the findings that CaO functions as calcium silicate component (CaO, SiO₂) which contribute to the improved strength, that an excellent sintered ceramic body can be obtained if the atomic ratio of Ca and P, Ca/P is kept in a range of 1.0 ~ 5.7 and at the same time, the contents of SiO₂, Na₂O, and MgO are kept at specific ranges, and that the application of the sol-gel method to the manufacture of said sintered body will further improve the quality of thus produced sintered ceramic bodies.

This invention offers sintered ceramic bodies in which the SiO₂ content is 20 ~ 70 wt%, the Ca to P atomic ratio, Ca/P is 1.0 ~ 5.7, the total content of SiO₂, P₂O₅ and CaO is greater than 70 wt%, and the contents of Na₂O and MgO are less than 2 wt% and 0.9 wt%, respectively.

In the sintered ceramic bodies of this invention, the SiO₂ content is kept in the range of 20 ~ 70 wt% (simply expressed as % hereafter), preferably at 30 ~ 40%. At below 20%, strength of the sintered body decreases and at above 70%, calcium phosphate crystal content including apatite decreases which results in the increase of crystals deriving from SiO₂.

The Ca to P atomic ratio, Ca/P is 1.0 ~ 5.7, preferably 1.5 ~ 3.7. If it is below 1.0, metaphosphate and pyrophosphate are produced, and at above 5.7, the apatite crystal content decreases. In this invention, the total content of three components mentioned above, i.e., SiO₂, CaO and P₂O₅ is kept at above 70%, preferably at 90%. The CaO and P₂O₅ contents can be flexible as long as they satisfy the conditions mentioned above. However, CaO at 10 ~ 70% and P₂O₅ at 5 ~ 40% are desirable.

In this invention, Na₂O and MgO should be kept at less than 2% and 0.9%, respectively. Preferably, inclusion of either component should be avoided. With Na₂O greater than 2%, strength of the sintered ceramic body decreases and the solubility in the human body increases. With MgO greater than 0.9%, magnesium silicate crystal tends to deposit.

In this invention, one or more than two components such as ZrO₂, Al₂O₃, TiO₂, B₂O₃, Y₂O₃, SiC, Si₃N₄, and AlN can be included at less than 30% in addition to the components mentioned above. Further, halogen compounds such as hydrochloric acid, hydrofluoric acid, hydrofluosilicic acid, calcium chloride and potassium fluoride, sulfides such as zinc sulfide, nucleus formation agents such as La₂O₃, CeO₂, SnO₂, Fe₂O₃, Li₂O, SrO, Nb₂O₅, Ta₂O₅, Ag, Au, Pt, Pd and Pb may be added at 0 ~ 10%.

The crystal structure of the sintered ceramic body of this invention which has the composition described above, consists of two components, i.e., crystalline and amorphous. The crystalline component preferably contains apatites (hydroxyapatite, oxygenated apatite, carbonated apatite, fluorinated apatite and chlorinated apatite) and calcium phosphate such as tricalcium phosphate (TCP). More preferably, it should contain wollastonite (CaO, SiO₂) that contributes to the strength of the sintered body. A small amounts of other crystals such as SiO₂ crystals (cristobalite, quartz, tridymite) or calcium pyrophosphate and calcium metaphosphate may also be contained. As for the amorphous component, amorphous components formed from three compounds of SiO₂, P₂O₅, CaO, alone or in combination, such as amorphous calcium phosphate, amorphous calcium silicate, amorphous silica, amorphous calcium silicophosphate are included. In this invention, among those crystals mentioned above, it is important to contain a large amount of apatite crystals.

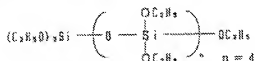
The sintered ceramic body of this invention can be manufactured by any method as long as it has the same compositions described above. However, the best method is the sol-gel method. Conventionally, glass has been manufactured by melting method or VAD (Vapor-Phase Axial Deposition Method). Glass ceramic has been then obtained by crystallization process of this glass. By sol-gel method, it can be synthesized at a low temperature and high purity materials can be obtained. Also, the method is not restricted by the vitrification ranges unlike the case with the melting method.

One preferred way is to follow the sintered ceramic body manufacturing method in which at least one of silicate esters shown by the general formula [I] is made into a gel in the presence of phosphorus compounds and calcium compounds, which is then dried, molded and sintered.



(R₁ ~ R₄ are hydrogen or radicals by the formula C_xH_{2x+1}(OC₂H₅)_y, - < where x = 1~5, y = 0~10 >. All of R₁ ~ R₄ need not be hydrogen. n = 0 ~ 20.)

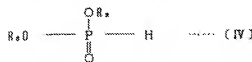
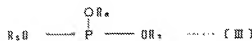
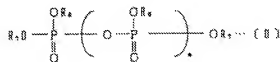
As for the silicate esters shown by the general formula [I], it is preferred that $R_1 \sim R_4$ are alkyl groups such as CH_3 , C_2H_5 , $n-C_3H_7$, $iso-C_3H_7$, $n-C_4H_9$ and $-C_2H_4OCH_3$. More preferably, $R_1 \sim R_4$ should be identical radicals. Although $n=0$ is preferred in this invention, condensates with $n=1 \sim 10$ are also usable. As the examples of silicate esters shown by the general formula [I], methyl silicate, ethyl silicate, *n*-propyl silicate, isopropyl silicate, *n*-butyl silicate and 2-methoxyethyl silicate and their 2 ~ 10 condensates can be listed. Of these, ethyl silicate, $Si(OC_2H_5)_4$, is available as Ethyl Silicate 28, and ethyl silicate with 5 mole (average) condensate:



is available as Ethyl Silicate 40 from Colcoat Company.

In this invention silicate ester concentration in the mixed solution is flexible. However, concentrations of 0.1 ~ 70%, preferably 10 ~ 40% as SiO_2 are favorable.

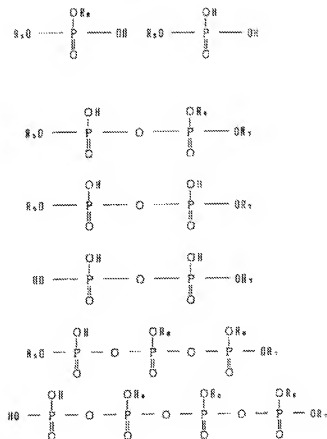
For phosphate compounds used in this manufacturing method, selecting at least one type of compound expressed by the general formulas [II], [III] or [IV] is preferred.



($R_5 \sim R_9$ are hydrogen, alkyl groups with 1 ~ 5 carbons, phenyl groups or aralkyl groups with 7 ~ 10 carbons, and $m=0 \sim 10$).

For phosphate esters of Formula [II], alkyl groups having 1 ~ 4 carbons are preferred for $R_6 \sim R_7$. Phenyl groups, benzyl groups are also favorable. For the range of m , $m=0 \sim 4$ is desirable. In addition, phosphate esters with all $R_6 \sim R_7$ being alkyl groups, phosphoric acid with all $R_6 \sim R_7$ being hydrogen and partial esters with both alkyl groups and hydrogen are also usable. As for metaphosphoric acid and meta phosphate esters expressed by the general formulas [III] and [IV], alkyl groups having 1 ~ 4 carbons are preferred. Also favorable are phenyl groups and benzyl groups. Desirable compounds are those expressed by formulas [III] and [IV] with $R_5 \sim R_9$ being methyl, ethyl, *iso*-propyl, *n*-butyl, phenyl and benzyl groups.

For the phosphate compounds of formula [II], at least one of $R_6 \sim R_7$ groups is hydrogen. However, for this invention, compounds in which not all $R_6 \sim R_7$ groups are hydrogen, are most desirable. Following compounds are listed as actual examples.



Only one or mixtures of more than two compounds can be used for the application. Here, $R_3 \sim R_2$, are the same as for formula [II] except that hydrogen is not included.

The phosphate esters listed above can be obtained easily by partially hydrolyzing analogous phosphate esters, by esterifying analogous phosphoric acids with alcohols, or by first reacting phosphorus pentoxide with alcohols and then hydrolyzing the reaction products.

Another essential component for this invention is calcium ion which can be prepared from calcium salts or calcium alcoxides. This is because addition of calcium is necessary to produce bioactive glass or glass ceramics. As the source of calcium ions, $\text{Ca}(\text{OR})_2$ (here, R is an alkyl group having 1-5 carbons), calcium nitrate, calcium acetate, calcium chloride, calcium hydroxide, calcium hydrogen citrate, calcium citrate, and calcium oxalate can be used.

Of these calcium ion sources, water soluble salts such as calcium nitrate, calcium acetate and calcium chloride are more favorable.

In addition to the elements mentioned above, elements that can become gel formation oxides may be included. As these elements, Al, Zr, Ti and B can be listed. In the same manner as for alkaline earth metals, these elements can be added in the form of metal alcoxides or water soluble salts. As for alcoxides, $Al(OR)_3$, $Zr(OR)_4$, $Ti(OR)_4$, and $B(OR)_3$ are desirable. The favorable amounts to be used are 0 ~ 30 wt% (as oxides) of the total amounts of elements (as oxides) constituting the gel. Similarly, ZrO_2 , Al_2O_3 , multi-, β -wollastonite, hydroxyapatite, SiC, Si_3N_4 , and AlN can be added and dispersed, in the forms of fine particles or whiskers, to the preparation solution before gelation. The suitable amounts of the powder or whiskers to be used are in the range of 0 ~ 30%.

In this invention, the raw materials are added in such a manner that the final products of the sintered ceramic body have the compositions that fall within the ranges specified above. Gelation of silicate esters is performed in the presence of phosphorus compounds and calcium compounds. The gelation reaction conditions are discussed below.

pH of the gelation reaction

In this invention, the gelation has to be performed at a neutral or an acidic condition where phosphorus component and calcium component mix well and gelate evenly. A pH below 4 is desirable.

If the phosphorus component used in this invention are phosphoric acid, phosphate partial esters, metaphosphoric acid and metaphosphate partial esters, pH adjustment reagents need not be added as these compounds are acidic. Otherwise, pH is adjusted with inorganic acids such as hydrochloric acid, nitric acid and sulfuric acid, or organic acids such as acetic acid, citric acid, and lactic acid. Phosphate esters and metaphosphate esters need the addition of these acidic materials. The pH may be maintained constant until the gelation is done, or to promote the gelation, the pH may be increased after silicate esters are partially hydrolyzed. Basic materials such as ammonium hydroxide, amines and formaldehyde may be used to increase the pH.

Solvents for reaction

Solvents suitable to dissolve silicate esters, phosphorus components and calcium components are water, alcohols such as methanol and ethanol, and their mixtures. The amount of water 1 ~ 15 times in mole basis vs. the amount of silicate esters is desirable for smooth hydrolysis.

Details of gel preparation methods

In this invention, multi-component gel is prepared according to the following methods.

- (i) Phosphorus compounds are added to silicate esters. After the silicate esters are partially hydrolyzed, calcium compounds are added to complete the gelation.
- (ii) After silicate esters are partially hydrolyzed, phosphorus compounds are added. Calcium compounds are then added to complete the gelation.
- (iii) Calcium compounds are added to silicate esters. After the silicate esters are partially hydrolyzed, phosphorus compounds are added to complete the gelation.
- (iv) After silicate esters are partially hydrolyzed, calcium compounds are added. Phosphorus compounds are then added to complete the gelation.
- (v) Silicate esters are added to a solution containing phosphorus compounds and calcium compounds to complete the gelation.
- (vi) Silicate esters, phosphorus compounds and calcium compounds are added simultaneously to complete the gelation.

Although the above-mentioned gelation, which involves hydrolysis and condensation polymerization, can be performed at ambient temperature, it may also be performed at a heated condition. If the temperature higher than the boiling point of solvents is desired, an autoclave may be used to perform hydrolysis and condensation polymerization under pressurized conditions.

Manufacture of sintered body

As a conventional sol-gel method to manufacture glasses, a method in which a sol is dried at a controlled evaporation rate to obtain dried gel without cracks, which can be sintered as is. The method is commonly used for manufacturing silica glasses. However, for multi-component gel of this invention, it is difficult to obtain dried gel without cracks. Sintering without creating cracks is even harder. Accordingly, a method in which dried gel is pulverized, heat-treated, molded and then sintered, is preferable.

Drying

Drying is done at 0 ~ 200°C, at atmospheric pressure or under a reduced pressure. Moist gel may be dried after pulverization, or pulverized after drying.

Heat treatment

The purpose of heat treatment is to remove residual alkoxy groups from Si, P and Ca atoms, further promote gel condensation polymerization and practically complete the reactions between components. The temperature range is 200 ~ 1000°C but 400 ~ 800°C is more favorable. At a temperature below 200°C, the effect of heat treatment will be inadequate. At above 1000°C, crystallization is promoted, resulting in inferior sintering.

Molding and sintering

Molding and sintering can be performed by method (i) ~ (iii) shown below.

- (i) Sintering is done at 800 ~ 1300°C at atmospheric pressure after the heat-treated powder is molded by a single axis press or a cold isostatic press (CIP).
- (ii) Heat-treated powder is sintered at 800 ~ 1300°C using a hot press machine.
- (iii) Molded heat-treated powder is directly pressed by a hot isostatic press (HIP), or the material sintered at atmospheric pressure is further pressed by a hot isostatic press (HIP).

In this invention, halogen compounds are added to prevent apatite crystals from decomposing into tricalcium phosphate (TCP) by high temperature heat at above 1150°C, and also prevent apatite from decomposing when sintering temperature is raised to obtain increased sinter density. For example, by adding halogen compounds at the manufacturing process of raw material powder before sintering, decomposition of hydroxyapatite is suppressed. Production of sintered bodies having apatite crystals is facilitated in this manner. Halogen compounds to be added are chloride or fluoride such as hydrochloric acid, calcium chloride, hydrofluoric acid, hydrofluosilicic acid, and calcium fluoride.

Halogen compounds can be added in the following manner: (1) The compounds are added to the solution before gelation. (2) The gel is soaked in the halogen compound solution before drying. (3) Dried powder or heat-treated powder is treated again with halogen salts solution. The desirable amount of halogen compounds to be added is 0.003 ~ 3% (as halogen ions) in relation to the total weight calculated as oxides.

[Effect of the invention]

This invention offers sintered ceramic bodies having superior biocompatibility and high strength.

Sintered ceramic bodies by this invention, therefore, can be usable for many applications such as synthetic tooth roots or synthetic bones.

In the following, this invention will be explained using the examples. However, this invention is not limited to these examples.

[Embodiments]

Embodiment 1

Silicate esters and phosphate compounds were mixed with 10 times as much water as the amount of silicate esters (in mole basis). The mixture was vigorously stirred at 45°C. One hour later, calcium nitrate solution (50% in water) was added to obtain a uniform solution. In Table 1, names of used silicate esters and phosphorus compounds are shown along with the ratio of these three ingredients calculated as oxide.

The solution was then sealed and let stand overnight at 45°C for gelation. The produced gel was dried for one week at 45°C with the seal removed. The dried gel was pulverized into powder, gradually heated at 20°C/hr to 500°C where it was kept for 10 hours for heat treatment. The heat-treated powder was wet-milled by a ball mill, molded and sintered for one hour using a hot press at 1200°C.

Sintered ceramic body thus obtained showed, by fluorescence X-ray analysis, a matching composition with the charged composition. Na₂O and MgO were not detected. A prism shaped piece, 3 x 4 x 30 mm, was prepared from the sintered ceramic body thus obtained. After surface polishing, bending strength was measured by three-point loading system. All results are summarized in Table 1.

Table 1

	Products of this invention						Products for comparison	
	1	2	3	4	5	6	1	2
Composition* SiO ₂ /CaO/P ₂ O ₅	46/38/16	27/51/22	58/31/11	55/27/17	38/48/14	40/46/13	41/25/34	50/43/7
Ca/P**	3	3	3.5	2	4.5	1.7	0.9	8
Silicate esters	ethyl silicate	ethyl silicate	ethyl silicate	ethyl silicate 40	ethyl silicate	methyl silicate	ethyl silicate	ethyl silicate
Phosphorus Component	monoethyl phosphate + diethyl phosphate (50/50)	triethyl meta-phosphate	ortho-phosphoric acid	monoethyl phosphate + diethyl phosphate (50/50)	monoethyl phosphate + diethyl phosphate (50/50)	ortho-phosphoric acid	ortho-phosphoric acid	ortho-phosphoric acid
Deposited crystals	apatite wollastonite	apatite wollastonite	apatite wollastonite	apatite	apatite wollastonite	apatite tricalcium phosphate	crystalline calcium pyrophosphate	wollastonite
Apatite X-ray diffraction peak intensity (cps)	1150	1360	1000	1240	800	1300	0	0
Bending strength, kg/cm ²	2000	1700	2200	1500	1800	1300	1000	1500

Note: * weight ratio ** atomic ratio

As is clear from Table 1, every product by this invention showed a high strength. All materials contained large amounts of apatite which is essential in forming chemical bonding with bones.

The products used for comparison did not show detectable amounts of apatite crystal deposit.

Embodiment 2

Gelation and heat treatment were performed in the same manner as for Embodiment 1 using ethyl silicate as a silicate ester. All conditions were the same except for those indicated in Table 2.

The heat-treated powder was wet-milled by a ball mill, molded by a cold isostatic press and sintered under atmospheric pressure at 1200°C. The deposited crystals are shown in Table 2. When partial phosphate esters were used instead of phosphoric acid, the results were more selective and more apatite crystals deposited.

Table 2

		Products of this invention			
		7	8	9	10
Composition*	SiO ₂	45	45	46	46
	CaO	34	34	38	38
	P ₂ O ₅	21	21	16	16
	MgO	0	0	0	0
	Na ₂ O	0	0	0	0
Ca/P**		2.0	2.0	3.0	3.0
Phosphorus Component		monoethyl phosphate + diethyl phosphate (50/50)	phosphoric acid	monoethyl phosphate + diethyl phosphate (50/50)	phosphoric acid
Deposited crystals		apatite	apatite tricalcium phosphate calcium pyrophosphate wollastonite	apatite wollastonite	apatite tricalcium phosphate wollastonite
Apatite X-ray diffraction peak intensity (cps)		1200	400	1100	600

Note: * weight ratio ** atomic ratio

Embodiment 3

Ethyl silicate 83.3g, 23.6 g of a mixture of monoethyl phosphate and diethyl phosphate (50/50), and 95 g of either water or hydrochloric acid solution (0.76 mole/L water) were mixed and stirred for 1 hour at ambient temperature. To this solution, 168.7 g of calcium nitrate solution (50% in water) was added and stirring was continued. Gelation was performed by leaving the solution in a sealed container overnight at 45°C. The composition of the gel was, $\text{SiO}_2 / \text{CaO} / \text{P}_2\text{O}_5 = 37 / 44 / 19$, by weight ratio. The gel was dried, with the container cover removed, for one week at 45°C. The dried gel was pulverized and then heated to 800°C at 20°C/Air. Heat treatment was performed by keeping it for 3 hours at 800°C.

The heat-treated powder was wet-milled by a ball mill, molded by a cold isostatic press and sintered under atmospheric pressure at 1100°C, 1150°C and 1200°C. The deposited crystals are shown in Table 3. When water was used, apatite started to decompose to tricalcium phosphate at around 1150°C. In contrast, when hydrochloric acid solution is used, the deposited crystal contained only apatite and wollastonite even at 1200°C, and decomposition of apatite to tricalcium phosphate was found to be negligible.

Table 3

Sintering temperature (°C)		1100	1150	1200
Deposited crystal	With water	apatite wollastonite	apatite tricalcium phosphate wollastonite	tricalcium phosphate wollastonite
	With hydrochloric acid solution	apatite wollastonite	apatite wollastonite	apatite wollastonite

Embodiment 4

An experiment was performed in the same manner as for Embodiment 3 using water for hydrolysis except that 2.4 g of hydrofluoric acid solution (10% in water) was added with cooling to the solution before gelation. When the heat-treated powder was sintered under atmospheric pressure at 1200°C, the deposited crystal showed apatite and wollastonite only. Decomposition of apatite to tricalcium phosphate was found to be negligible.

Embodiment 5

An experiment was performed in the same manner as for Embodiment 3 using hydrochloric acid solution (0.17 mole/L) for hydrolysis. After molding and sintering under atmospheric pressure at 1200°C, the deposited crystal showed apatite and wollastonite only. Decomposition of apatite to tricalcium phosphate was barely detected.

Comparative example 3

A mixture of 30 g of amorphous silica powder, 24.4 g of calcium hydrogen phosphate dehydrate and 28.7 g of calcium carbonate (corresponding to: $\text{SiO}_2 / \text{CaO} / \text{P}_2\text{O}_5 = 16 / 38 / 16$) was pre-baked at 1000°C. The pre-baked powder was submitted to melting for 1 hour at 1600°C. However, even melt could not be obtained as unmelted residues remained.

Written Amendment

April 26, 1988

To: Kunio Ogawa, Director-General of Patent Office

1. Case Identification: 1987 (Showa 63 nen) Patent Application No. 51783
2. Title of the Invention: Sintered Ceramic Body and the Method of Manufacture Thereof
3. Person to File Amendment: {676} Lion Corporation
Relationship to Case: Patent Applicant
4. Agent: {5995} Minoru Nakamura, Patent Attorney *[stamped with his name]*
5. Date of Order of Amendment: Voluntary
6. Parts Amended: In "Details of the Invention" -- Paragraph entitled "Detailed Description of the Invention"
7. Contents of Amendment:
 - (1) Details of the Invention, p. 11, 5th line from the bottom:
"0.1 ~40%" is corrected to [0.1 ~ 40 wt%, preferably 2 ~ 30%].
 - (2) In the same page, 2nd line from the bottom:
"phosphate compounds" is corrected to [phosphorus compounds].
 - (3) In the same part, p. 24: Table 1 is corrected as follows.

*[stamped: Formality Examiner, Ueda]**[stamped: Patent Office, 63. 4. 27. Application Office No. 2, Yamaguchi]*

Table 1

	Products of this invention						Products for comparison	
	1	2	3	4	5	6	1	2
Composition* SiO ₂ -CaO-P ₂ O ₅	46/38/16	27/31/22	58/31/11	55/27/17	38/48/14	40/46/13	41/25/34	50/43/7
Ca/P**	3	3	3.5	2	4.5	1.7	0.9	8
Silicate esters	ethyl silicate	ethyl silicate	ethyl silicate	ethyl silicate 40	ethyl silicate	ethyl silicate	ethyl silicate	ethyl silicate
Phosphorus Component	monoethyl phosphate + diethyl phosphate (50/50)	triethyl meta-phosphate	ortho-phosphoric acid	monoethyl phosphate + diethyl phosphate (50/50)	monoethyl phosphate + diethyl phosphate (50/50)	ortho-phosphoric acid	ortho-phosphoric acid	ortho-phosphoric acid
Deposited crystals	apatite wollastonite	apatite wollastonite	apatite wollastonite	apatite	apatite wollastonite	apatite uscalcium phosphate	crystaline calcium pyro-phosphate	wollastonite
Apartite X-ray diffraction peak intensity (cps)	1150	1360	1000	1240	800	1300	0	0
Bending strength, kg/cm ²	2000	1700	2200	1500	1800	1300	1000	1500

Note: * weight ratio ** atomic ratio